# 2 Analysis of Variations in Ozone & Ozone Precursors

## 2.5 Ozone Carryover and Day-of-Week Phenomena Based on Data from Ozonesondes, Aircraft Measurements, and Ozone Lidar during SCOS97

### 2.5.1 Abstract

Does ozone carryover aloft affect day-of-the-week phenomena? Given substantially limited and intermittent data aloft that are currently available, both in time and in space, we cannot resolve this question. As ozone levels have declined, the relative contribution of carryover may also have declined. However, day-of-week variations in the amounts and proportions of ozone precursors could have implications for day-of-week variations in ozone aloft that are not directly proportional to the day-of-week variations observed in surface ozone concentrations. If ozone formation at ground level is VOC-limited and ozone formation aloft is $NO_X$-limited, the relative differences in VOC and $NO_X$ emissions from weekdays to weekends could result in ozone concentrations aloft being poorly related to the ozone concentrations measured at ground level. Another question is how does carryover of ozone and aged pollutants aloft affect day-of-the-week ground level ozone phenomena. If surface measurements are low due to ozone quenching by fresh NO emissions and substantial ozone is formed above the immediate surface layer where air monitoring instruments are typically located, then the daily increased mixing of the atmosphere during the morning and early afternoon hours could transport substantial amounts of ozone and aged pollutants into the surface layer. The limited analysis presented in this sub-chapter suggests that carryover of ozone does have day-of-week influences. Polluted air aloft can routinely affect ground level ozone concentrations. At many locations, peak ozone concentrations are typically the lowest of the week on Monday. This occurs despite the fact that the fresh emission of ozone precursors on Monday is very similar to those on other weekdays, which have higher ozone concentrations. If ozone formation aloft is NOX-limited, then it may well be that the amount of ozone formed aloft on Sundays is the lowest of the week despite ozone concentrations near the ground, where ozone formation appears to be VOC-limited, being the highest of the week. If ozone aloft is a significant portion of the ozone measured at the surface during periods of vertical mixing, then the lower amount of ozone aloft that is available for carryover to contribute to Monday's surface level ozone would be less. The smaller ozone aloft carryover from Sunday would cause the peak ozone concentration on Monday to be lower than other weekdays despite comparable fresh emissions. As indicated by the analyses below, some polluted layers are at least two days old and can routinely impact ozone concentrations at ground level. On one occasion, the contribution of ozone concentrations aloft to ozone concentrations at ground level was 20 parts per billion volume (ppbV), or 30 percent of the ozone loading at ground level.

## 2.5.2 Introduction

In the early 1990s, Saturday was the day-of-the-week with the highest peak concentration of ambient ozone in the South Coast Air Basin (SoCAB) [*Austin & Tran*, 1999; *Blier et al.*, 1999; *Blier et al.*, 1996]. By the late 1990s, Sunday appears to have replaced Saturday as the day-of-the-week with the highest peak concentration of ambient ozone in the SoCAB (*Austin & Tran*, 1999; *Blier et al.*, 1999). Various potential factors contributing to the Ozone Weekend Effect have been hypothesized. One hypothesis is that carryover of ozone and other pollutants aloft affect or influence ozone photochemistry at ground level. For this mechanism to be a contributor to the ozone weekend effect, carryover of ozone aloft needs to occur routinely and the pollution aloft must be sufficiently low in altitude to be "tapped" by the increased vertical mixing of the atmosphere during the morning and early afternoon. This analysis examines data collected by means of ozonesondes, aircraft, and lidar during the 1997 Southern California Ozone Study (SCOS97) to address the potential for carryover aloft and to gain some insight into how atmospheric processes cause air aloft to be different from air observed with the routine surface-based measurements.

## 2.5.3 Methodology

During SCOS97, ozonesondes (balloons with instruments measuring total oxidant (via chemical reaction with potassium iodine), temperature, and relative humidity) were launched from seven locations. Potassium iodine instruments respond to not only ozone – the primary constituent of photochemical smog – but also, to some extent, to other oxidants such as nitrogen dioxide ($NO_2$), nitric acid ($HNO_3$), atomic oxygen (O), nitrate radical ($NO_3$), peroxyacetylnitrate (PAN), dinitrogen petoxide ($N_2O_5$), etc. The potassium iodide measurement method used in ozonesondes can also be negatively impacted by some compounds such as sulfur dioxide ($SO_2$). .

The University of Southern California's (USC) Hancock Foundation Building, located south of Central Los Angeles, was one of the ozonesonde release sites. Balloons were launched at 0200, 0800, 1400, and 2000 Pacific Daylight Time (PDT). The USC site is located 4 miles southwest of LANM. The USC data provide a snapshot-in-time view of the vertical profile of ozone concentrations and meteorological conditions aloft. The USC ozone balloon data have passed "level 1" quality guidelines (*Fujita* et. al., 1999).

During SCOS97, the CARB contracted for aircraft measurements of meteorological and air quality parameters, including ozone, nitric oxide (NO), and total oxides of nitrogen ($NO_Y$). Downward and upward spirals were performed during flights to estimate vertical profiles of the atmospheric parameters. In some instances, spirals were performed multiple times during the day at the same location to provide an indication of how atmospheric conditions changed and the potential atmospheric processes at work. A few vertical profiles of ozone, NO, NOY, and HNO3 (estimated) made at the VanNuys Airport are provided to illustrate common atmospheric

processes. The morning spirals occurred around 6 a.m. PDT while the afternoon spirals occurred around 4 p.m. PDT.

During SCOS97, the National Oceanic and Atmospheric Administration (NOAA) operated an ozone lidar during the intensive operational periods to provide nearly continuous vertical profiles of ozone and aerosols above the El Monte Airport. This lidar uses beam splitting to allocate the laser power into different height bins and thereby enhancing the dynamic range of measurements. The effective range of this ozone lidar is from 100 meters above ground level (AGL) to 200+ meters AGL. Because the errors in this remote sensing device are cumulative, the measurement uncertainties increase with altitude. Figure 2.5-1 provides an uncertainty estimate of the measurements with altitude. In general, the uncertainty in the measurements with this lidar increased rapidly above 1500 to 2000 meters AGL depending on the particular day. Although this lidar is not a reference air quality measurement, it does provide a reasonable picture of relative vertical and temporal differences in ozone concentrations and provides good insight into the atmospheric processes that are occurring but not well captured by instantaneous measurements such as aircraft and ozonesondes. Furthermore, lidars provide a true vertical profile whereas the aircraft spirals and ozonesondes incorporate some horizontal and temporal variations into their vertical profile estimates.

### 2.5.4 Results & Discussion

#### 2.5.4.1 Ozonesondes

During SCOS97, ozone data collected with a balloon provided a snap shot of the entirety of the aloft profile. Looking at these snapshots in view of the evolution of ground level concentrations provided another piece of anecdotal analysis to focus on multi-day carryover events.

It is conceptually convenient to separate the closest layer to the ground (up to 500 to 700 meters agl) as the compartment in the atmosphere most susceptible to interaction with the ground-based emissions and atmospheric chemistry associated with these emissions. Due to the cessation of photochemical production of ozone, the influence of the nocturnal boundary conditions, and the nighttime emissions of nitrogen oxide, ozone concentrations in this reservoir layer may be reduced to very low concentrations nocturnally. During the day, much of ozone buildup related to that day's atmospheric chemistry fills this compartment first. For further convenience we have called this layer the “reservoir” (Figure 2.5-2).

There are a series of layers of ozone above the reservoir (from 500-700 up to 3,000-4,000 meters agl) that can be viewed for conceptual convenience as one alpha layer. These layers are influenced by flow of ozone from the reservoir (daytime) and from above the alpha layer and in turn can influence ozone in the reservoir. Ozone concentrations are not significantly reduced at night because nighttime ground deposition and nitrogen oxide emissions have no significant impact on these layers. Thus, the alpha layer may exist at high concentrations for several days. Although

their interaction with the reservoir and their consequent impact on ground level ozone concentrations depend primarily on the meteorological factors, the ozone concentration load they contain depends primarily on reservoir ozone formation processes occurring then and up to several days before.

There are yet a third series of ozone layers above the alpha layer (from 3,000-4,000 up to 6,000+ meters agl) that can be viewed for conceptual convenience as one beta layer. These layers can be influenced by flow of ozone from the alpha and reservoir layers and in turn may influence the alpha and reservoir layers; more importantly they have a regional nature and speak more to the background ozone concentrations. Although there is less complexity above the boundary layer where the flow is driven by synoptic scale events, the three-dimensional nature of ozone layers aloft in the complex southern California Bight is the result of land-sea interactions that play a critical role in developing regional meteorology and atmospheric chemistry. Designation of these layers is only for convenience and cannot reflect the full complexity of ozone aloft phenomena.

Nevertheless, a series of USC balloon snapshots of the ozone vertical profile is indicative of interaction of the alpha layers with ground levels. In particular, these interactions are noted for the August 22nd to 23rd high ozone episode (Friday to Saturday). By the early morning hours (0200) before Saturday, August 23rd, the alpha layer had perhaps 60 to 80 ppbV of ozone within it while the reservoir was essentially exhausted. While the reservoir grew by atmospheric chemistry of morning emissions (0800 hours snapshot), boundary conditions improved to permit more mixing and by 1400 hours the alpha layer seemed to have mixed with the reservoir. There were indications that carryover affected the ground level concentrations (Figure 2.5-3 through Figure 2.5-7).

The USC snapshots from September 4 (Thursday) to 6 (Saturday) indicate that such carryover can take place over more than one day. A narrow alpha layer containing roughly 80 ppbV of ozone began on Thursday and was reinforced during Thursday, existed during Friday and weakened somewhat but did not mix down, and finally mixed down on Saturday and was entirely exhausted contributing to a peak of 66 ppbV at LANM. Carryover from Thursday affected Saturday's ground level ozone concentrations (Figure 2.5-8 through Figure 2.5-13).

The limited analyses presented here do not account for the fact that photochemical processes aloft are rather like ground level processes in that ozone, reactive organic gases, and nitrogen species are part of a complex set of chemical interactions that continue away from emission sources. These limited analyses are two-dimensional snapshots of three-dimensional phenomena that encompass the entirety of the southern California Bight and includes land-sea interactions and air parcel transport processes. Furthermore, the implications of the analyses may be limited because the meteorological conditions during the summer of 1997 were not typical of normal summer conditions due to a strong El Niño. Nevertheless, there is evidence that ozone in layers aloft affected ground level concentrations and that such carryover aloft can persist more than one day.

### 2.5.4.2 Aircraft Spirals

Morning and afternoon spirals are presented in Figures 2.5-14 through 2.5-17 for air quality parameters above VanNuys Airport on August 22 and 23, 1997. On the morning of August 22, note the fresh NO emissions almost completely scavenge the ozone below 500 m MSL. Ozone concentrations rise from near zero at 500 m to more uniform values aloft at 750 m MSL. By afternoon, pollutant layering is occurring with ozone concentrations elevated (80 –140 ppb). Note that while NO concentrations are much smaller than in the morning and ozone concentrations are above regional background levels, the ozone concentrations are still being suppressed 20-30 ppb below 500 m MSL.

On the morning of August 23, the spiral terminated above 500m MSL and NO concentrations were near 0 ppb. The ozone profile shows no obvious quenching and ozone aloft is in the 50 – 60 ppb range. In the afternoon, NO concentrations once again are near 0 ppb and the ozone concentration is steady at ~100 ppb up to about 1200 m MSL. As the higher oxidized $NO_X$ products decline to near 0 ppb at 1400 m MSL, the ozone also declines to global background levels (20 - 30 ppb).

### 2.5.4.3 Ozone Lidar

Time-height ozone profiles are presented for two days to illustrate dynamic features of atmospheric processes that can occur on a regular basis. The main points the authors would like the reader to remember. First, the surface-based measurements routinely made with monitoring network are strongly impacted by emission sources at ground level (i.e., primarily ubiquitous motor vehicles) and do not characterize ozone conditions aloft throughout the day (not even during times of day with good vertical mixing because of the impact of fresh emissions). Second, the surface-based measurements are only representative of conditions in the lowest 10 to a couple hundred of meters AGL and there is ozone formation throughout several hundreds of meters above the surface layer. The large mass of ozone in this thicker layer of the atmosphere is routinely mixed down to the surface of the earth during the day.

The first profile is for Monday, September 29, 1997 and is presented in Figure 2.5-18. Notice the blue color in the lower left-hand corner of the time-height profile. The blue indicates low ozone concentrations in the surface layer and this is likely due to ozone quenching by NO emissions during the night. Remember that ozone is a photochemical pollutant and is only formed when sunlight is present. The ozone concentrations measured at the surface by the routine monitoring network do not necessarily characterize the ozone concentrations aloft. In fact, they seldom do because fresh NO emissions are continuously suppressing the ozone in the surface layer. Note in this figure that the ozone concentrations aloft begin increasing after sunrise but before vertical mixing of the atmosphere causes air aloft to begin mixing down to the surface (around 9:30 a.m.). Also note that the peak ozone concentrations were between 500 and 1200 meters AGL but that the ozone aloft never appreciably mixed down to the surface. However, advection of the polluted

layer further inland could impact surface readings where the vertical mixing of the atmosphere is stronger or transport into the mountains could occur.

The second profile is for Saturday, August 23, 1997 and is presented in Figure 2.5-19. The data presented here shows a deeper depleted layer in the morning, likely due to a thicker marine layer of air. However, high ozone concentrations develop later in the day from a short distance above the ground to a thousand meters or more above the ground. Note the ozone quenching still occurring in a shallow layer near the ground during the mixing period. Once again, the ozone aloft is significantly higher than observed with traditional surface-based monitors.

### 2.5.5 Conclusions

There are indications that for a source area during SCOS97, carryover of ozone aloft had day-of -week influences and that, without the effect of carryover aloft, ground level ozone concentrations would be less than otherwise. Setting aside additional chemistry in aloft layers, there are also indications that layers of ozone aloft, some at least 2 days old, affected ground level concentrations. It also appears that ozone quenching by NO occurs during all hours of the day when fresh NO emissions are present. Furthermore, it appears that ozone concentrations aloft can begin increasing after sunrise despite no fresh emissions being mixed up to that altitude by then.

### 2.5.6 Recommendations

This type of data is critical for evaluating regional air pollution transport at local atmospheric processes affecting the formation and destruction of ozone. With recent assessments of trans-national air pollution transport (to and from Mexico and from the People's Republic of China), these analyses are even more relevant and important for California. Continuous ozone aloft measurements using light detection and ranging during several ozone seasons would provide a database to properly conduct these analyses of transport and atmospheric processes aloft. Continuous measurements of hydrocarbons and nitrogenous species during several ozone offshore, on-shore, and aloft in the region would also help this type of analysis.

### 2.5.7 References

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